REDUCTION OF NITRIC OXIDE BY LOW-RANK COAL CHARS

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INTRODUCTION

The increasingly stringent environmental legislation requires efforts to find more effective and inexpensive pollution control systems. Removal of NO_x from both stationary and mobile sources is the subject of very intense research and development. Selective catalytic reduction (SCR) is commercially available technology [1,2]. However, when excess oxygen is present in the exhaust gases the state-of-the-art catalyst is not effective for removing NO_x [3-5].

Carbon is known to be an effective adsorbent and catalyst in the simultaneous removal of SO_x and NO_x [6-8]. Reducing agents such as NH_3, CO, H_2 or hydrocarbons with an alumina- or titania-supported catalyst are used [3,9-10]. The problem with this technology is the need to introduce a reducing agent to the feed. The use of inexpensive coal-based chars which are gradually consumed can be an interesting solution because no additional reductant is required. Chars produced from lignites are known to exhibit high catalytic activity for the reduction of NO with ammonia [11] and recently a 'calcined' char from a subbituminous coal was used to remove NO_x with the assistance of microwave energy [12].

In this paper, low-rank coal chars are used to remove NO_x from an oxygen-rich atmosphere. The effects of both pyrolysis temperature and inorganic impurities naturally present in coals are studied.

EXPERIMENTAL

Four low-rank coals, two lignites and two subbituminous coals, were selected for direct NO reduction in the presence of O_2. Table 1 shows the PSOC number, the ASTM rank and selected inorganic components in the coals. Eight chars were obtained by pyrolyzing the coals in a tube furnace at 500 and 700 °C (N_2, 80 mL/min, 1h). An additional char was prepared by pyrolyzing one of the lignites at 900 °C.

The kinetics of the $NO+O_2$/carbon reaction was studied at atmospheric pressure in a fixed-bed quartz microreactor connected to a quadrupole mass spectrometer (VG QUADRUPOLE). Temperature-programmed reaction ($^{15}NO+O_2$, 10 °C/min, T_{max}=500 °C) and isothermal reaction experiments were carried out in the following environments: (i) 0.5% $^{15}NO/Ar$, (ii) 5% O_2/Ar, and (iii) 0.5% $^{15}NO/5\% O_2/Ar$. Temperature-programmed desorption (TPD) runs were also conducted (He, 20 °C/min, T_{max}=900 °C) before and after isothermal reaction in the various mixtures.

RESULTS AND DISCUSSION

Temperature-programmed reaction (TPR) experiments. Figure 1 shows the TPR curves, %NO reduction *vs.* reaction temperature, for the three chars obtained from lignite 1422. Chars 1422/700 and 1422/900 exhibit somewhat different behavior from that of the low-temperature char (1422/500): NO reduction maximum at low temperature (T<200 °C) and a lower NO reduction capacity at high temperature (T>200 °C). As can be concluded from Figure 2, this characteristic low-temperature TPR profile is only exhibited by chars prepared from lignites 1422 and 1548, which have the highest potassium and sodium content (see Table 1). Similar low-temperature profiles were found for activated carbon loaded with potassium [13,14].

The analysis of reaction products evolved during the low-temperature reaction stage reveals some significant differences with respect to the potassium-loaded activated carbons. The quantity of N_2 evolved is much smaller than the quantity of NO retained (~5%); in other words, non-dissociative NO chemisorption seems to be the main phenomenon occurring at the low temperatures [13,14]. Subsequent desorption of thus retained NO gives rise to the negative values shown at intermediate temperatures in Figures 1 and 2.

The fact that the low-temperature TPR behavior described above is observed only for chars pyrolyzed at 700 and 900 °C means that important changes take place during the coal pyrolysis step. The theoretical temperature of reduction of potassium oxide (K_2O) by carbon (graphite) is 825 °C [15]; furthermore, it is well known [16] that reduced potassium species can spread over the surface and thus achieve a high degree of dispersion. Obviously, these two phenomena are more important at higher pyrolysis temperatures; consequently, potassium-catalyzed NO adsorption [17] becomes more pronounced.

In the high-temperature region, where a continuous increase in NO reduction is observed (Figures 1 and 2), pyrolysis temperature has the opposite effect: the low-temperature char exhibits a higher activity for NO reduction than chars pyrolyzed at higher temperatures (1422/700 and 1422/900). Analysis of the reaction products evolved shows that NO reduction is accompanied by evolution of N_2, N_2O and CO_2.

Char 1422/500 thus shows the highest activity for NO reduction. In agreement with the well known effects of pyrolysis temperature on char reactivity [18-20], it also has the highest reactivity in O_2 (see also Table 2). For example, the temperature at which the O_2/C reaction starts (during a TPR experiment) is the lowest. Also, the ignition temperature has been used in the literature as a good index to compare the reactivity of carbons in O_2 [21]; lower ignition temperature was observed for char 1422/500 (~305 °C) than for char 1422/700 (~340 °C). On the other hand, a higher ignition temperature and no substantial difference was observed for the two chars prepared from coal 1547 (~380 °C for both 1547/500 and 1547/700), which has the lowest content of potassium and sodium. This is not a surprising result of course. Alkali metals are very effective catalysts for carbon oxidation reactions [22]. Furthermore, a correlation between the NO reduction capacity of a char and its reactivity in O_2 has been discussed in detail recently [17].

It was thus of interest to monitor the nature and quantity of carbon-oxygen surface complexes formed on the surface of room-temperature-air-exposed coal chars before NO reduction. The CO_2 and CO evolved in a TPD experiment is a convenient measure of surface complexes present on the chars [23]. The quantity of CO_2 and CO evolved by the low-temperature char 1422/500 (1605 and 650 µmol/g C) is higher than that evolved from high-temperature chars 1422/700 and 1422/900 (902 and 963 µmol/g C, and 369 and 113 µmol/g C, respectively); furthermore, the chars obtained from subbituminous coals, 1547/500 and 1547/700, yield less CO_2 and CO (703 and 928 µmol/g C, and 549 and 386 µmol/g C, respectively).

The different effects of pyrolysis temperature in the low-temperature *vs.* high-temperature region imply that different active sites are involved in the two regimes. At low temperatures, the activity for NO reduction is governed by the catalyst active sites; at higher temperatures, the reactivity of the char (i.e., the number of carbon active sites) appears to control the NO reduction behavior. A similar conclusion was reached in our previous TPR study using an activated carbon loaded with different amounts of potassium: the low-temperature profile was determined by catalyst loading and dispersion, but no differences were observed at higher temperatures, where carbon reactivity controls the NO reduction capacity [14].

Isothermal reaction experiments. Isothermal reaction experiments were performed in three different atmospheres: NO+O_2, NO and O_2. After reaction (for ca. 60 minutes), a TPD experiment was also performed.

Figure 3 shows the evolution of the % NO reduction curve with time for all chars pyrolyzed at 500 °C and also for chars 1422/700 and 1422/900. Table 2 summarizes the kinetic data for NO reduction after 1 hour in both atmospheres (NO and NO+O_2), as well as the reactivity in oxygen (5% O_2, balance Ar) and the level of carbon consumption (% burnoff). The isothermal behavior observed supports the conclusions based on the TPR study: (a) chars from lignites 1422 and 1548 have a higher capacity for NO reduction than chars prepared from subbituminous coals, and (b) the low-temperature chars show the highest activity in the NO+O_2/C reaction. Table 2 also reveals that the high NO reduction level is maintained by chars 1422/500 and 1548/500 and that a reasonable carbon consumption level is achieved. The main reaction products are N_2 and CO_2, with some N_2O being evolved (N_2O/N_2=0.15), but CO is not detected.

The activity data in the absence of oxygen confirm the important enhancement of NO reduction capacity in an oxygen-rich atmosphere [24,17]. The degree of enhancement is larger for the 500 °C chars than for the 700 °C chars. It is also more important for chars obtained from the two lignites. The reactivity in O_2 seems to be the key to the understanding of these effects: chars that exhibit the highest increase in NO reduction (1422/500 and 1548/500) also have the highest reactivity in oxygen. Again, the analogy between NO reduction by carbon and the carbon/O_2 reaction is made apparent.

The results discussed above are in agreement with some recent studies of Tomita and coworkers [25] and with our previous proposal about the role of oxygen in NO reduction [17]. This can be summarized succinctly as follows:

$$2C_f + O_2 \longrightarrow 2C(O) \qquad (1)$$

$$2C(O) \longrightarrow CO_2 + C_f \qquad (2)$$

$$C(O) \longrightarrow CO\,(+\,C_f) \qquad (3)$$
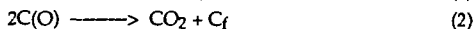
Upon desorption of CO_2 and CO, a larger number of free actives sites (C_f) on the carbon surface is produced than in the absence of O_2; it is these 'nascent' sites which increase char's activity for NO reduction. By comparing columns 3, 5 and 7 in Table 2, we conclude that, despite the much higher propensity of chars to react with O_2, the fraction of carbon consumed by NO (column 8) can be quite high. (It is this number which may require some additional optimization in pursuit of commercial viability of this novel approach to NO_x reduction.) Mochida et al. [26] recently concluded also that the active sites in carbon/NO/O_2 system are created by liberation of CO and CO_2, in contrast to their earlier assumption [7] that the active sites are the carbon-oxygen surface complexes.

Finally, analysis of the species evolved during TPD after isothermal reaction also provides valuable information. Evolution of N_2 is not significant, suggesting both that N_2 is produced primarily according to the reaction $2NO + 2C_f = 2C(O) + N_2$ [17] and that the concentration of $C(N)$ surface complexes is not very high. This conclusion is in agreement with our previous results using activated carbons [13-14,17,27]. In Figure 4, the increase in the amount of CO_2 evolved after the NO+O_2/C reaction indicates that some oxygen is retained on the surface during the NO/C reaction. This surface oxygen (or oxygen-containing species) can be retained by either the catalyst or the char. The fact that the CO_2 desorption curves show a peak with a maximum at ~560 °C suggests that CO_2 is captured by K_2O thus forming a carbonate. The formation of K_2CO_3 has also been suggested by García-García et al. [28] after the NO+O_2/C reaction in similar potassium-loaded char samples; its decomposition, during subsequent TPD, exhibited a maximum at ~600 °C. The CO curves show a maximum at ~700 °C, which can be due to partial reduction of metallic oxides present in the ash (e.g., K_2O, Na_2O, Fe_2O_3) by the char. (CO peaks with maxima at ~750 and ~800 °C were observed during TPD of K- and Fe-loaded activated carbons [13,27].) In support of the above interpretation is the finding that TPD curves for chars 1422/700 and 1422/900 show a better defined CO_2 peak after NO+O_2/C and O_2/C reactions, even though a lower amount of CO_2 is evolved (in agreement with the fact that these chars are less active for NO reduction): a more reduced and better dispersed potassium species seems to be obtained after pyrolysis at 700 and 900 °C. Another interesting result from this series of TPD experiments is that the amount of CO_2 retained by the char after NO+O_2/C reaction increases with increasing pyrolysis temperature: 4% of CO_2 evolved is captured (as K_2CO_3) by char 1422/500, while 18 and 55% are captured by chars 1422/700 and 1422/900, respectively.

ACKNOWLEDGEMENTS

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Table 1. Properties of Coals

PSOC No.	ASTM rank	ASTM ash yield (wt %)	Inorganic element analysis (wt %)
1422	Lignite	9.49	Na, 0.73; K, 0.11; Ca, 1.4; Fe, 0.81
1548	Lignite A	6.37	Na, 0.66; K, 0.05; Ca, 1.8; Fe, 0.61
1547	Subbituminous	9.85	Na, 0.12; K, 0.05; Ca, 1.3; Fe, 0.85
1546	Subbituminous	4.80	Na, 0.25; K, 0.05; Ca, 0.60; Fe, 0.20

Table 2. NO Reduction Data at 350 °C for Different Coal Chars

Char	Pyrolysis yield (wt %)	% NO reduced		% Burnoff		Reactivity in O_2 (h^{-1})*	F**
		$NO+O_2$	NO	$NO+O_2$	NO		
1422/500	45	54	12	19.5	0.3	0.20	0.13
1422/700	37	34	18	4.0	0.4	0.06	0.25
1422/900	32	0	-	1.1	-	0.01	0.23
1548/500	47	53	12	21.0	0.5	0.23	0.09
1548/700	40	35	15	4.0	0.4	0.04	0.37
1547/500	54	17	0	3.4	0.3	0.04	0.21
1547/700	52	11	10	2.6	0.2	0.02	0.22
1546/500	52	24	-	11.0	-	0.13	0.20
1546/700	45	11	-	4.3	-	0.05	0.27

*integrated value, based on carbon consumption over the 60-minute period.
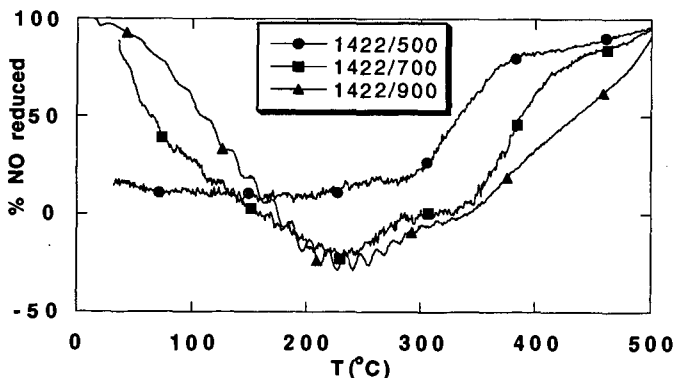**F = fraction of carbon consumed by NO (in the $NO+O_2/C$ reaction).

Figure 1. TPR profiles (0.5% NO, 5% O_2, balance Ar) for chars obtained from lignite 1422: effect of pyrolysis temperature.
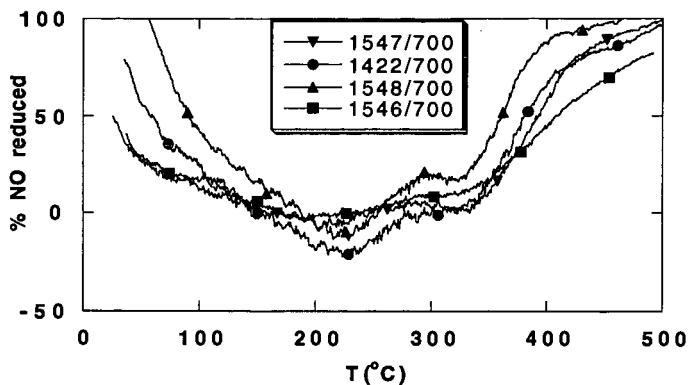
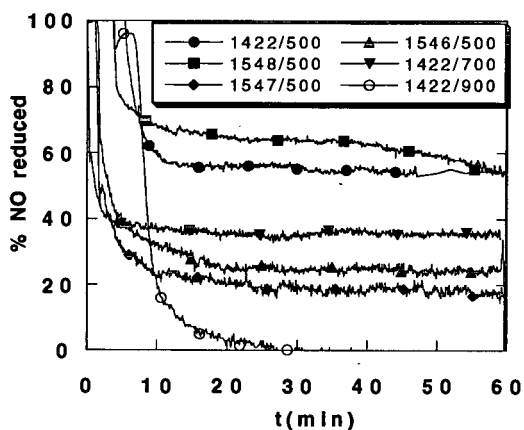**Figure 2.** TPR profiles (0.5% NO, 5% O_2, balance Ar) for chars pyrolyzed at 700 °C: effect of coal rank.

Figure 3. Effect of pyrolysis temperature on the kinetics of the NO+O_2/C reaction (350 °C; 0.5% NO, 5% O_2, balance Ar).
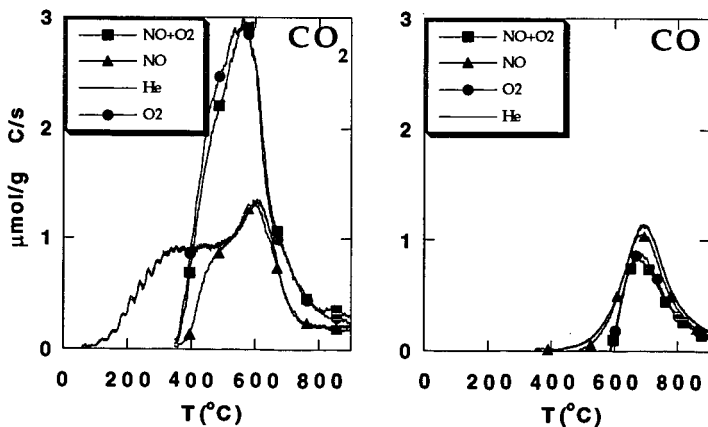

Figure 4. TPD profiles for sample 1422/500 before (He) and after reaction in NO+O_2, NO and O_2.